

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Mark D. Elkovich et al.)	
)	Group Art Unit: 1751
Serial No.:	10/797,298)	
)	
Filed:	March 9, 2004)	Examiner: Thomas, Jaison P
)	
For:	ELECTRICALLY CONDUCTIVE)	
	COMPOSITIONS AND METHOD)	
	OF MANUFACTURE THEREOF)	

VIA ELECTRONIC FILING

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

APPEAL BRIEF

Please find enclosed a copy of an appeal brief pursuant to the communication received from the USPTO dated 05/10/2007.

I. REAL PARTY IN INTEREST

The real party in interest in this appeal is the General Electric Company.

II. RELATED APPEALS AND INTERFERENCES

There are no related appeals or interferences known to Appellants, Appellants' legal representatives, or the assignee that will directly affect, be directly affected by, or have a bearing on the Board's decision in the pending appeal.

III. STATUS OF THE CLAIMS

Claims 1 - 42 are pending in the application. Claims 25 - 40 and 42 have been withdrawn from consideration. Claims 1 - 17, 20 - 24, and 41 stand rejected. Claims 18 and 19 are objected to. Claims 1 - 42, as they currently stand, are set forth in Appendix A. Appellants hereby appeal the rejection of Claims 1 - 17, 20 - 24, and 41.

IV. STATUS OF THE AMENDMENTS

No amendments have been filed subsequent to the rejection of March 13, 2007. All prior amendments have been entered.

V. SUMMARY OF CLAIMED SUBJECT MATTER

Articles made from polymeric resins are commonly utilized in material-handling and electronic devices such as packaging film, chip carriers, computers, printers and photocopier components where properties such as electrostatic dissipation or electromagnetic shielding are desirable. As electronic devices become smaller and faster, their sensitivity to electrostatic charges is increased and hence it is generally desirable to utilize polymeric resins that have been modified with electrically conducting fillers to provide improved electrostatically dissipative properties. In a similar manner, it is desirable to modify polymeric resins so that they can provide improved electromagnetic shielding while simultaneously retaining some or all of the advantageous mechanical properties of the polymeric resins.

Electrostatic dissipation (hereafter "ESD") is defined as the transfer of electrostatic charge between bodies at different potentials by direct contact or by an

induced electrostatic field. Electromagnetic shielding (hereafter "EM shielding") effectiveness is defined as the ratio (in decibels) of the proportion of an electromagnetic field incident upon the shield that is transmitted through it. Conductive fillers such as graphite fibers derived from pitch and polyacrylonitrile having diameters larger than 2 micrometers are often incorporated into polymeric resins to improve the electrical properties and achieve ESD and EM shielding. However, because of the large size of these graphite fibers, the incorporation of such fibers generally causes a decrease in the mechanical properties such as impact. Therefore it would be desirable to develop conductive polymeric compositions, which while providing adequate ESD and EM shielding, can retain their mechanical properties.

The invention is directed towards a composition which is electrically conductive, having an electrical volume resistivity less than or equal to about 10^8 ohm-cm, a notched Izod impact strength greater than or equal to about 5 kilojoules/square meter, and a Class A surface finish. The composition comprises a polymeric resin, an electrically insulating nanosized dispersion agent and carbon nanotubes. The polymeric resin may be selected from a wide variety of thermoplastic resins, blend of thermoplastic resins, or blends of thermoplastic resins with thermosetting resins. The polymeric resin may also be a blend of polymers, copolymers, terpolymers, or combinations comprising at least one of the foregoing polymeric resins. The carbon nanotubes used in the composition may be single wall carbon nanotubes (SWNTs), multiwall carbon nanotubes (MWNTs) or vapor grown carbon fibers (VGCF). The nanosized dispersion agents are electrically non-conducting. They are generally ceramic particles such as metal oxides, highly crosslinked silicones, polyhedral oligomeric silsesquioxanes (POSS) macromers, metal carbides, nanoclays and the like, which have maximum particle sizes less than or equal to about 1200 nm.

It is believed that the present composition has numerous advantages. The nanosized dispersion agent promotes the dispersion of the carbon nanotubes within the polymeric resin with minimal degradation to the aspect ratio of the carbon nanotubes. This permits the use of smaller amounts of carbon nanotubes in the composition while obtaining levels of electrical conductivity comparable with the use of larger quantities of carbon nanotubes. The use of smaller amounts of carbon nanotubes allows for the retention of intrinsic properties of the polymeric resin such as ductility, flexibility, impact

strength, and the like. Such compositions can be advantageously utilized in computers, electronic goods, semi-conductor components, circuit boards, or the like which need to be protected from electrostatic dissipation. They may also be used advantageously in automotive body panels both for interior and exterior components of automobiles that can be electrostatically painted if desired.

In addition, an article is described which comprises the inventive composition.

Independent Claim 1 is directed to an electrically conductive composition comprising a polymeric resin, a nanosized dispersion agent that is electrically non-conducting, and carbon nanotubes, wherein the composition has an electrical volume resistivity less than or equal to about 10^8 ohm-cm, and a notched Izod impact strength greater than or equal to about 5 kilojoules/square meter.

Support for the polymeric resin can be found on page 3, paragraph [0010] to page 4, paragraph [0012]. Support for the carbon nanotubes can be found on page 4, paragraph [0013] lines 1-3. Support for the electrically non-conducting nanosized dispersion agent can be found on page 13, paragraph [0036], lines 1-3. Support for the volume resistivity less than or equal to about 10^8 ohm-cm can be found on page 3, paragraph [0009], line 3. Support for the notched Izod impact strength greater than or equal to about 5 kilojoules/square meter can be found on page 3, paragraph [0009], line 4.

Independent Claim 41 is directed to an article manufactured from the inventive composition.

Support for the article can be found on page 22, paragraph [0059], lines 2-10.

VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

- 1) Claims 1-17, 20-24, and 41 stand rejected under 35 U.S.C. § 102(b) as being anticipated by International PCT Application Publication No. WO 97/15935 to Shibuta, hereafter “Shibuta”.
- 2) Claims 4-8 and 11-14 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Shibuta, in view of Applied Nanotech Inc. (ANI) webpage (<http://www.applied-nanotech.com/cntproperties.htm>), hereafter “ANI”.

VII. ARGUMENT

1. **Claims 1-17, 20-24, and 41 are patentable under 35 U.S.C. § 102(b) over Shibuta.**

In making the rejection, the Examiner has stated the following:

“With respect to the Shibuta rejections, applicant argues that Shibuta requires electrically conductive metal oxides whereas as the instant claims are directed towards non-conductive nanodispersion agents. Applicant further argues that the non-conductive powders that are disclosed in Shibuta are coated with a conductive surface and cites sections of Shibuta to support this position. The Examiner respectfully disagrees with the Applicant, because as stated in the prior office action, Shibuta teaches a composition that contains a polymeric resin, nanotubes, and metal oxides which are equivalent to the compositions that are claimed and disclosed in the Applicant’s specification. The metal oxides include titanium oxide and zinc oxide (see pg. 7, lines 11 and 12) used in Shibuta are identical to the nanodispersion agents disclosed in Applicant’s specification and claims (see instant Claim 23 and Specification, pg. 14, para. 0040). Therefore the nanodispersion agents of the instant claims and the metal oxides of Shibuta are identical and mere reference to claimed set as “non-conductive” and the prior art set as “conductive” does not change this fact. Further, the Examiner respectfully is unclear as to where Applicant believes the metal oxides of Shibuta are coated with a conductive surface. The Examiner has checked the sections cited by Applicant in his Remarks (particularly citations of Shibuta at pg. 7, lines 29-34 and pg. 8, lines 9-10) in the Shibuta PCT reference and has found no support for the statements that the said metal oxides from Shibuta are coated with any conductive surfaces.”

(Office Action dated March 13, 2007, pages 2-4.) Applicants respectfully disagree.

To anticipate a claim under 35 U.S.C. § 102, a single source must contain all of the elements of the claim. *Lewmar Marine Inc. v. Barient, Inc.*, 827 F.2d 744, 747, 3 U.S.P.Q.2d 1766, 1768 (Fed. Cir. 1987), *cert. denied*, 484 U.S. 1007 (1988).

Shibuta teaches a transparent electrically conductive film having a surface resistivity of 10^2 - 10^{10} ohm per square, an overall light transmittance of at least 70%, and a haze value of at most 20%. The film comprises an organic or inorganic transparent matrix having dispersed therein 0.01%-1wt% of hollow carbon microfibers and 1%-40wt% of an electrically conductive metal oxide powder (such as antimony-doped tin oxide) with an average primary particle diameter of 0.5 μm or smaller (Shibuta, abstract.)

By emphasizing the use of electrically conductive particles, Shibuta teaches away from the presently claimed electrically non-conductive particles.

The Examiner has stated that the nanodispersion agents of the instant claims and the metal oxides of Shibuta are identical and mere reference to claimed set as “non-conductive” and the prior art set as “conductive” does not change this fact. The Examiner has further stated that the metal oxides include titanium oxide and zinc oxide (see pg. 7, lines 11 and 12) used in Shibuta are identical to the nanodispersion agents disclosed in Applicant’s specification and claims (see instant Claim 23 and Specification, pg. 14, para. 0040). Applicants respectfully submit that zinc oxide along with titanium oxide are generally known to be dielectric materials. Applicants respectfully cite International PCT Application Publication No. WO 97/15934 (see Appendix B) to Shibuta, hereafter “Shibuta ‘934”, filed on the same date as Shibuta. Shibuta ‘934 teaches an electrically conductive polymer composition comprising an organic polymer, hollow carbon microfibers, and an electrically conductive white powder (such as TiO₂ powder coated with antimony-doped tin oxide or aluminum-doped zinc oxide powder) (Shibuta ‘934, abstract.) Shibuta discloses:

“examples of a surface-coated conductive white powder (2) are nonconductive white powders such as titanium oxide, zinc oxide, silica, aluminum oxide, magnesium oxide, zirconium oxide, a titanate of an alkali metal (such as potassium titanate), aluminum borate, barium sulfate, and synthetic fluoromica with the surface thereof coated with a transparent or white electrically conductive metal oxide such as ATO, AZO, or ITO. Titanium oxide is most preferred as the nonconductive white powder because its coloring ability is greatest, but others can be used alone or in combination with titanium oxide. ATO and AZO are preferred as the conductive metal oxide for surface coating because they have good covering properties.”

(emphasis added, Shibuta ‘934, page 8, lines 9-20.) Thus, Applicants respectfully assert that Shibuta ‘934 teaches that titanium oxide and zinc oxide are non-conductive, and in order to render them conductive they are coated with an electrically conductive metal oxide. Applicants respectfully submit that Shibuta’s oversight at disclosing titanium oxide and zinc oxide as conductive materials is a direct contradiction of Shibuta ‘934, and also a contradiction of the fact that titanium oxide and zinc oxide are both known to be dielectric materials. Applicants respectfully submit that Shibuta’s mischaracterization

of titanium oxide and zinc oxide as conductive materials may stem from the teaching that they can be rendered electrically conductive by doping them with a different element to produce an oxygen deficiency, for example, Al and In to zinc oxide, and Nb and Ta to titanium oxide (Shibuta, page 7, lines 3-9.)

Thus, Applicants respectfully assert that titanium oxide and zinc oxide are not conductive as evidenced by Shibuta '934 and by Applicants' Specification. Shibuta does not teach all the elements of Applicants' independent claim 1, specifically that the nanosized dispersion agent is electrically non-conducting. Shibuta, thus, does not anticipate the instant claims, and the instant claims are patentable over Shibuta.

2. Claims 4-8 and 11-14 are patentable under 35 U.S.C. § 103(a) over Shibuta in view of ANI.

Shibuta is discussed above. ANI teaches physical, mechanical, and other properties of carbon nanotubes (ANI, and links therein.) ANI does not remedy the lack of teaching of an electrically non-conducting dispersion agent in Shibuta.

For an obviousness rejection to be proper, the Examiner must meet the burden of establishing a *prima facie* case of obviousness, i.e., that all elements of the invention are disclosed in the prior art; that the prior art relied upon, coupled with knowledge generally available in the art at the time of the invention, contain some suggestion or incentive that would have motivated the skilled artisan to modify a reference or combined references; and that the proposed modification of the prior art had a reasonable expectation of success, determined from the vantage point of the skilled artisan at the time the invention was made. *In re Fine*, 5 U.S.P.Q.2d 1596, 1598 (Fed. Cir. 1988); *In Re Wilson*, 165 U.S.P.Q. 494, 496 (C.C.P.A. 1970); *Amgen v. Chugai Pharmaceuticals Co.*, 927 U.S.P.Q.2d, 1016, 1023 (Fed. Cir. 1996).

Applicants respectfully assert that in view of the remarks above regarding Shibuta, and in light of the disclosure of Shibuta '934, there is no teaching or suggestion in Shibuta, ANI, or the combination of both references to use a nanosized dispersion agent that is electrically non-conducting as required by Applicants' independent claim 1. Thus, the combination of the cited references does not teach or suggest all the elements of

independent claim 1, a prima facie case of obviousness has not been established, and the instant claims are patentable over Shibuta in view of ANI.

VIII. CLAIMS APPENDIX

APPENDIX A

1. (Previously Presented) An electrically conductive composition comprising:
 - a polymeric resin;
 - a nanosized dispersion agent that is electrically non-conducting; and
 - carbon nanotubes, wherein the composition has an electrical volume resistivity less than or equal to about 10^8 ohm-cm, and a notched Izod impact strength greater than or equal to about 5 kilojoules/square meter.
2. (Original) The composition of Claim 1, wherein the carbon nanotubes are single wall carbon nanotubes, multiwall carbon nanotubes, vapor grown carbon fibers or a combination comprising at least one of the foregoing types of carbon nanotubes.
3. (Original) The composition of Claim 1, wherein the carbon nanotubes have an inherent electrical conductivity of about 10^4 Siemens/centimeter.
4. (Original) The composition of Claim 1, wherein the composition has an electron-transport mechanism that is ballistic.
5. (Original) The composition of Claim 1, wherein the carbon nanotubes exist in the form of ropes of at least about 10 carbon nanotubes prior to processing.
6. (Original) The composition of Claim 1, wherein the carbon nanotubes exist in the form of ropes of at least about 100 carbon nanotubes prior to processing.
7. (Original) The composition of Claim 1, wherein the carbon nanotubes exist in the form of ropes of at least about 1000 carbon nanotubes prior to processing.
8. (Original) The composition of Claim 1, wherein the carbon nanotubes exist in the form of ropes of at least about 10000 carbon nanotubes prior to processing.

9. (Original) The composition of Claim 1, wherein the carbon nanotubes comprise up to about 80 wt% impurities, wherein the impurities are iron, iron oxides, yttrium, cadmium, nickel, cobalt, copper, soot, amorphous carbon, multi-wall carbon nanotubes, or a combination comprising at least one of the foregoing impurities.

10. (Original) The composition of Claim 2, wherein the single wall carbon nanotubes comprise up to about 80 wt% impurities, wherein the impurities are iron, iron oxides, yttrium, cadmium, nickel, cobalt, copper, soot, amorphous carbon, multi-wall carbon nanotubes, or a combination comprising at least one of the foregoing impurities.

11. (Original) The composition of Claim 1, wherein the carbon nanotubes are metallic, semi-conducting, or a combination comprising at least one of the foregoing carbon nanotubes.

12. (Original) The composition of Claim 11, wherein the carbon nanotubes comprise about 1 to about 99.99 wt% metallic carbon nanotubes.

13. (Original) The composition of Claim 11, wherein the carbon nanotubes comprise about 1 to about 99.99 wt% semi-conducting carbon nanotubes.

14. (Original) The composition of Claim 1, wherein the nanotubes are armchair nanotubes, zigzag nanotubes, or a combination comprising at least one of the foregoing nanotubes.

15. (Original) The composition of Claim 1, wherein the carbon nanotubes comprise about 1 to about 80 wt% impurities.

16. (Original) The composition of Claim 1, wherein the polymeric resin is a blend of polymers, a copolymer, a terpolymer or a combination comprising at least one of the foregoing polymeric resins.

17. (Original) The composition of Claim 16, wherein the polymeric resin has a phase separated morphology and wherein a substantial proportion of the carbon nanotubes are present in a single phase of the blend.

18. (Original) The composition of Claim 1, wherein the carbon nanotubes are derivatized with functional groups.

19. (Original) The composition of Claim 1, wherein the carbon nanotubes are derivatized with functional groups either on a side-wall or on a hemispherical end.

20. (Original) The composition of Claim 1, wherein the carbon nanotubes have no hemispherical ends attached thereto or have at least one hemispherical end attached thereto.

21. (Original) The composition of Claim 1, wherein the nanosized dispersion agents are metal oxides, polyhedral oligomeric silsesquioxanes macromers, highly crosslinked silicone nanosized agents, metal carbides, nanoclays having an average particle size of less than or equal to about 1200 nanometers.

22. (Original) The composition of Claim 1, wherein the nanosized dispersion agents is a metal oxide of an alkali earth metals, an alkaline earth metals, a transition metals or a combination comprising at least one of the foregoing metal oxides.

23. (Original) The composition of Claim 22, wherein the metal oxide is a aluminum oxide, magnesium oxide, calcium oxide, copper oxide, zinc oxide, titanium oxide or a combination comprising at least one of the foregoing oxides.

24. (Original) The composition of Claim 1, comprising about 0.01 to about 20 wt% nanosized dispersion agents based on the total weight of the composition.

25. (Withdrawn) A method for manufacturing a composition comprising:

blending a polymeric resin, nanosized dispersion agent and carbon nanotubes, wherein the composition has an electrical volume resistivity less than or equal to about 10^8 ohm-cm, and a notched Izod impact strength greater than or equal to about 5 kilojoules/square meter.

26. (Withdrawn) The method of Claim 25, wherein the blending comprises melt blending, solution blending or combinations comprising at least one of the foregoing methods of blending.

27. (Withdrawn) The method of Claim 25, wherein the polymeric resin is synthesized from monomers, dimers, trimers or a combination comprising at least one of the foregoing monomers, dimers or trimers during the process of blending.

28. (Withdrawn) The method of Claim 25, wherein the carbon nanotubes are sonicated in the presence of the monomer prior to the polymerization of the polymer.

29. (Withdrawn) The method of Claim 25, wherein the polymeric resin is semi-crystalline or amorphous and has a molecular weight of about 100g/mole to about 1,000,000 g/mole.

30. (Withdrawn) The method of Claim 25, wherein the blending involves the use of shear force, extensional force, compressive force, ultrasonic energy, electromagnetic energy, thermal energy or combinations comprising at least one of the foregoing forces and energies and is conducted in processing equipment wherein the aforementioned forces are exerted by a single screw, multiple screws, intermeshing co-rotating or counter rotating screws, non-intermeshing co-rotating or counter rotating screws, reciprocating screws, screws with pins, barrels with pins, screen packs, rolls, rams, helical rotors, or combinations comprising at least one of the foregoing.

31. (Withdrawn) The method of Claim 25, wherein the blending involves extrusion and wherein the single wall carbon nanotubes or the nanosized dispersion agent or both are fed downstream as a masterbatch into the extruder.

32. (Withdrawn) The method of Claim 25, wherein the composition is further subjected to ultradrawing in the unaxial direction utilizing draw ratios of about 2 to about 1,000,000.

33. (Withdrawn) The method of Claim 25, wherein the composition is further stressed uniaxially or biaxially to produce a film having a thickness of about 0.01 micrometers to about 5000 micrometers.

34. (Withdrawn) The method of Claim 25, wherein the composition is further supercooled to a temperature of about 1°C to about 100°C below the melting point after the blending for a time period of about 2 minutes to about 2 hours.

35. (Withdrawn) The method of Claim 25, wherein the blending comprises melt blending or solution blending, and wherein the blending utilizes a fluid in the liquid state, the gaseous state, the supercritical state or combinations comprising at least one of the foregoing states.

36. (Withdrawn) The method of Claim 25, wherein the energy utilized for the blending is an amount of about 0.1 kWhr/kg to about 10 kWhr/kg.

37. (Withdrawn) The method of Claim 25, wherein the nanosized dispersion agents are metal oxides, polyhedral oligomeric silsesquioxanes macromers, metal carbides, highly crosslinked silicone nanosized agents, nanoclays having an average particle size of less than or equal to about 1200 nanometers.

38. (Withdrawn) The method of Claim 25, wherein the nanosized dispersion agents is a metal oxide of an alkali earth metals, an alkaline earth metals, a transition metals or a combination comprising at least one of the foregoing metal oxides.

39. (Withdrawn) The method of Claim 25, wherein the metal oxide is a aluminum oxide, magnesium oxide, calcium oxide, copper oxide, zinc oxide, titanium oxide or a combination comprising at least one of the foregoing oxides.

40. (Withdrawn) The method of Claim 25, wherein the composition comprises about 0.01 to about 20 wt% of the nanosized dispersion agents based on the total weight of the composition.

41. (Original) An article manufactured from the composition of Claim 1.

42. (Withdrawn) An article manufactured by the method of Claim 25.

IX. EVIDENCE APPENDIX

No additional evidence is submitted herein.

X. RELATED PROCEEDINGS APPENDIX

There have been no related proceedings in connection with this appeal brief. As a result there are no decisions rendered by a court or the Board pursuant to paragraph (c)(1)(ii) of this section.

XI. CONCLUSION

Thus the Examiner's rejections of claims 1-17, 20-24, and 41 under 35 U.S.C. § 102(b) and of claims 4-8 and 11-14 under 35 U.S.C. § 103(a) should be reversed, and Claims 1-17, 20-24, and 41 should be allowed.

In summary, the references cited by the Examiner (PCT Application Publication No. WO 97/15935 and Applied Nanotech Inc. (ANI) webpage) do not disclose or suggest the following features of independent claim 1, in particular:

- a nanosized dispersion agent that is electrically non-conducting.

In view of the foregoing, Appellants respectfully submit that all of the claims are allowable and the application is in condition for allowance. Appellants respectfully request reversal of the outstanding rejections and allowance of this application.

In the event the Examiner has any queries regarding the submitted arguments, the undersigned respectfully requests the courtesy of a telephone conference to discuss any matters in need of attention.

If there are any additional charges with respect to this Appeal Brief, please charge them to Deposit Account No. 50-1131.

Respectfully submitted,

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APPENDIX B

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01B 1/24, 1/20		A1	(11) International Publication Number: WO 97/15934 (43) International Publication Date: 1 May 1997 (01.05.97)
(21) International Application Number: PCT/JP96/03051		(81) Designated States: AU, CA, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
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(71) Applicants (<i>for all designated States except US</i>): MITSUBISHI MATERIALS CORPORATION [JP/JP]; 1-5-1, Otemachi, Chiyoda-ku, Tokyo 100 (JP). HYPERION CATALYSIS INTERNATIONAL [US/US]; 38 Smith Place, Cambridge, MA 02138 (US).			
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(54) Title: ELECTRICALLY CONDUCTIVE POLYMER COMPOSITION

(57) Abstract

A white or colored electrically conductive polymer composition is provided using carbon fiber. The composition comprises a moldable organic polymer dispersed therein (a) at least 0.01 wt.% and less than 2 wt.% of hollow carbon microfibers having an outer diameter of 3.5 - 70 nm and an aspect ratio of at least 5, (b) 2.5 - 40 wt.% of an electrically conductive white powder (such as TiO₂ powder coated with antimony-doped tin oxide, or aluminum-doped zinc oxide powder), and optionally (c) a colorant for coloration.

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ELECTRICALLY CONDUCTIVE POLYMER COMPOSITION

Technical Field

This invention relates to an electrically conductive polymer composition and particularly to a white or colored 5 conductive polymer composition which can be used to form electrically conductive filaments (including conjugate fibers containing such filaments), films, sheets, three dimensional articles, and similar products. A conductive shaped product obtained from the composition according to this invention can 10 be employed in antistatic mats, materials for shielding electromagnetic waves, IC trays, in construction materials such as floor and ceiling materials for clean rooms, sealing materials, tiles, and carpets, in packaging for film, dust-free clothing, and conductive parts of office equipment (rollers, 15 gears, connectors, etc.).

Background Art

It is well known to disperse an electrically conductive material in an electrically insulating polymer to prevent static charge or other purposes and obtain an electrically 20 conductive polymer (see, for example, Japanese Patent Publication (Kokoku) No. 58-39175). As electrically conductive materials which are admixed with polymers, ionic or nonionic organic surfactants, metal powders, electrically conductive metal oxide powders, carbon black, carbon fibers, and the like 25 are generally used. There are dispersed in a polymer by melting and kneading to form an electrically conductive polymer composition, which is shaped to obtain an electrically conductive article having a volume resistivity of 10^9 - 10^{10} $\Omega \cdot \text{cm}$.

30 It is also known that use of a material having a large aspect ratio such as flakes or whiskers as the conductive material can provide a polymer with electrical conductivity using a relatively small amount. This is because a conductive material having a large aspect ratio increases the number of 35 contact points between the material for the same unit weight, so it is possible to obtain electrical conductivity using a smaller amount.

However, a conventional electrically conductive polymer composition has problems with respect to stability at high temperatures (heat resistance and dimensional stability), moldability, and color.

- 5 For example, when an organic surfactant is used as the conductive material, the heat resistance is poor, and the electrical conductivity is easily influenced by humidity. An inorganic conductive material is usually in the form of spherical particles, so it is necessary to mix a large quantity
10 exceeding 50 wt% based on the total weight of the composition, so the physical properties of the polymer worsen, and its moldability into filaments or films is decreased.

- Even with flake-shaped or whisker-shaped conductive materials having a large aspect ratio, it has been
15 conventionally necessary to use them in an amount exceeding 40 wt% based on the total weight of the composition. When such a large amount of an electrically conductive material is mixed in a polymer, a directionality (anisotropy) develops at the time of shaping, and the moldability and electrical conductivity are
20 worsened.

- In the case of carbon black, if the amount required to impart electrical conductivity (generally at least 10 wt% based on the total weight of the composition) is used, the composition becomes black, and a white or colored formed
25 product can not be obtained.

- Carbon fibers, and particularly graphitized carbon fibers, have good electrical conductivity, and it has been attempted to disperse carbon fibers into a polymer as a conductive material. In particular, carbon fibers formed by vapor phase growth
30 method (pyrolysis method) and graphitized, if necessary, by heat treatment, and which are hollow or solid with a fiber diameter of from 0.1 μm to several μm have high electrical conductivity and have attracted attention as a conductive material. However, even with such carbon fibers, when they are
35 admixed in an amount sufficient to impart electrical conductivity, the polymer composition ends up becoming black.

Recently, carbon microfibers with a far smaller fiber diameter than carbon fibers formed by the vapor phase growth

method (referred to below as hollow carbon microfibers) have been developed. See, for example, Japanese Patent Publications (Kokoku) Nos. 3-64606 and 3-77288, Japanese Patent Laid-Open (Kokai) Applications Nos. 3-287821 and 5-125619, and U.S. Patent No. 4,663,220. These microfibers have an outer diameter of less than 0.1 μm , and normally on the order of several nanometers to several tens of nanometers. As they have a slenderness of the nanometer order, they are also referred to as nanotubes or carbon fibrils. They are usually extremely fine hollow carbon fibers having a tubular wall formed by stacking of layers of graphitized carbon atoms in a regular arrangement. These hollow carbon microfibers are used as a reinforcing material in the manufacture of composite materials, and it has been proposed to mix them into various types of resins and rubber as a conductive material. (See, for example, Japanese Patent Laid-Open (Kokai) Applications Nos. 2-232244, 2-235945, 2-276839, and 3-55709).

In Japanese Patent Laid-Open (Kokai) Application No. 3-74465, a resin composition is disclosed which is imparted electrical conductivity and/or a jet black color and which is formed from 0.1 - 50 parts by weight of carbon fibrils (hollow carbon microfibers) in which at least 50 wt% of the fibers are intertwined to form an aggregate, and 99.9 - 50 parts by weight of a synthetic resin. In that application, it is described that it is preferred to use at least 2 parts by weight of hollow carbon microfibers to impart electrical conductivity, and when imparting only a jet black color, the amount used is preferably 0.1 - 5 parts by weight.

As described above, carbonaceous conductive materials have excellent heat stability and can impart electrical conductivity to a polymer by using in a relatively small amount, but they have the drawback that they end up blackening the polymer. Uses for conductive polymers include antistatic mats, electromagnetic wave shield materials, IC trays, building materials, and packaging for film, and in each of these uses, there is a strong need to be able to freely perform coloring, either for reasons of visual design or to permit differentiation of products (such as in the case of IC trays).

An object of the present invention is to provide an electrically conductive polymer composition which has excellent electrical conductivity, heat resistance, and moldability, and which can be used to form a white or colored product by any 5 melt-molding methods including melt spinning, melt extrusion, and injection molding.

A more specific object of the present invention is to provide a white or freely colored electrically conductive polymer composition which uses a carbonaceous conductive 10 material and which can be used to form a product of a desired color.

Disclosure of Invention

As stated above, when a carbonaceous conductive material (carbon black, carbon fibers, etc.) is blended with a polymer, 15 the composition as a whole ends up black, so until now, it has been thought that it would be difficult to use a carbonaceous conductive material to form a white or colored (with a color other than black) conductive product, and it was never attempted to make one.

20 The present inventors investigated the characteristics of the above-described hollow carbon microfibers as an electrically conductive material. It was found that because microfibers are extremely slender, they can impart electrical conductivity to a polymer when mixed in an amount of at least 25 0.01 wt% which is far less than the amount used of conventional carbon fibers. Furthermore, it was found that when the content is less than 2 wt%, the amount of blackening of the polymer by the carbon fibers decreases and can be substantially entirely hidden by the simultaneous presence in the polymer of a white 30 powder to obtain a white conductive formable composition. Furthermore, it was found that by mixing a coloring agent in the white composition, a desired color can be obtained, thereby attaining the present invention.

Accordingly, the present invention resides in a white 35 electrically conductive polymer composition comprising hollow carbon microfibers and an electrically conductive white powder dispersed in a moldable organic polymer. In general, it contains, with respect to the total weight of the composition,

at least 0.01 wt% and less than 2 wt% of hollow carbon microfibers and 2.5 - 40 wt% of an electrically conductive white powder.

By further admixing a coloring agent (colored pigment, 5 paint, etc.) with the white conductive polymer composition, an electrically conductive polymer composition having a desired color can be obtained.

In the present invention, two types of electrically conductive materials, (A) hollow carbon microfibers, which are 10 conductive fibers, and (B) a conductive white powder, are dispersed in a moldable polymer. The use of the hollow carbon microfibers is expected to blacken the polymer, but when the amount is less than 2 wt%, by the simultaneous presence of the white powder, the blackening is counteracted, and a visually 15 white composition can be obtained. As a result of imparting electrical conductivity by means of the hollow carbon microfibers, the amount of the electrically conductive white powder can be limited to a relatively small amount of 2.5 - 40 wt% necessary for whitening (hiding of the black color). If 20 whitening is performed in this manner, and if a coloring agent is further added, coloring can be freely performed.

Best Mode for Carrying Out the Invention

The hollow carbon microfibers used in the present invention as conductive fibers are extremely fine, hollow 25 carbon fibers obtained by the vapor phase deposition method (a method in which a carbon-containing gas such as CO or a hydrocarbon is catalytically pyrolyzed in the presence of a transition metal-containing particles whereby the carbon formed by pyrolysis grows on the particles as starting points of 30 growth to form fibers). In general, the outer diameter of the hollow carbon microfibers is less than 0.1 μm (100 nm), and preferably they have an outer diameter of 3.5 - 70 nm and an aspect ratio of at least 5. Preferred hollow carbon microfibers are carbon fibrils described in U.S Patent No. 35 4,663,230 or Japanese Patent Publications (Kokoku) Nos. 3-64606 and 3-77288, or hollow graphite fibers described in Japanese Patent Laid-Open (Kokai) Application No. 5-125619.

Particularly preferred hollow carbon microfibers for use

in the present invention are those commercially available from Hyperion Catalysis International, Inc. (USA) under the trademark Graphite Fibril. These are graphitic hollow microfibers with an outer diameter of 10 - 20 nm (0.01 - 0.02 5 μm), an inner diameter of at most 5 nm (0.005 μm), and a length of 100 - 20,000 nm (0.1 - 20 μm).

These hollow carbon microfibers have less ability to produce black coloration or to conceal than normal carbon black, and due to their extremely large aspect ratio of 5 - 10 1000, they can be bent. Preferably, the hollow carbon microfibers have a volume resistivity in bulk of at most 10 $\Omega\cdot\text{cm}$ (measured under a pressure of 100 kg/cm²), and more preferably at most 1 $\Omega\cdot\text{cm}$.

The electrically conductive white powder used in this 15 invention performs the two functions of imparting electrical conductivity and whiteness to the polymer. However, for electrical conductivity, the hollow carbon microfibers are also present, so the amount of powder which is added can be limited to the amount necessary to produce whitening. The conductive 20 white powder preferably has a volume resistivity of at most 10⁴ $\Omega\cdot\text{cm}$ (measured under a pressure of 100 kg/cm²) and a whiteness of at least 70, and more preferably it has a volume resistivity of at most 10³ $\Omega\cdot\text{cm}$ and a whiteness of at least 80.

Here, the whiteness refers to the value W(Lab) calculated 25 using the following equation from the values of L, a, and b measured by the Hunter Lab colorimetric system:

$$W(\text{Lab}) = 100 - [(100 - L)^2 + a^2 + b^2]^{1/2}$$

The shape of the conductive white powder is not critical. For example, it can be from completely spherical to roughly 30 spherical powder (collectively referred to below as roughly spherical powder), or it can be flake-shaped or whisker-shaped powder having a large aspect ratio (collectively referred to below as high aspect ratio powder). However, spherical white powder generally has a greater ability to conceal, so 35 preferably at least a portion of the conductive white powder is roughly spherical powder.

The average particle size of the conductive white powder (the corresponding diameter in the case of roughly spherical

powder, and the average value of the largest dimension in the case of flake-shaped or whisker-shaped high aspect ratio powder) is preferably 0.05 - 10 μm and more preferably 0.08 - 5 μm . More specifically, for a roughly spherical white powder,
5 the average particle diameter is preferably at most 1 μm , and more preferably at most 0.5 μm . For a flake-shaped or whisker-shaped white powder with an aspect ratio of 10 - 200, the average particle diameter can be up to 10 μm or more, and preferably it is at most 5 μm .

10 If the average particle diameter of the electrically conductive white powder is less than 0.05 μm , the powder becomes transparent and the whiteness decreases, and in the case of the below-described surface coating-type electrically conductive white powder, the amount of surface coating increases, and this may lead to a decrease in whiteness. On the other hand, if the average particle diameter exceeds 1 μm for roughly spherical powder and exceeds 10 μm for high aspect ratio powder, particularly when the product which is formed is a film or filaments, the thickness or diameter of which is
15 generally several μm to several hundred μm , the smoothness of the film tends to decrease or breakage during melt spinning tends to occur.
20

When the electrically conductive white powder has an average particle diameter within the above-described range, the relative surface area thereof is generally in the range of 25 0.5 - 50 m^2/g and preferably 3 - 30 m^2/g for roughly spherical powder and is 0.1 - 10 m^2/g and preferably 1 - 10 m^2/g for high aspect ratio powder.

The electrically conductive white powder used in this invention can be (1) a white powder which itself is electrically conductive, or (2) a non-conductive white powder the surface of which is coated with a transparent or white electrically conductive metal oxide (referred to below as a surface coated conductive white powder).
30

35 An example of (1) is a white metal oxide powder, the electrical conductivity of which is increased by doping with another element. Specific examples include aluminum-doped zinc oxide (abbreviated as AZO), antimony-doped tin oxide

(abbreviated as ATO), and tin-doped indium oxide (abbreviated as ITO). The white powder having electrical conductivity by itself preferably has a such a particle diameter that the whiteness is at least 70. For example, when the particle 5 diameter of ATO or ITO becomes small, the particles become transparent and the whiteness tends to decreases. For this reason, a preferred conductive white powder is AZO having a high whiteness.

Examples of a surface-coated conductive white powder (2) 10 are nonconductive white powders such as titanium oxide, zinc oxide, silica, aluminum oxide, magnesium oxide, zirconium oxide, a titanate of an alkali metal (such as potassium titanate), aluminum borate, barium sulfate, and synthetic fluoromica with the surface thereof coated with a transparent 15 or white electrically conductive metal oxide such as ATO, AZO, or ITO. Titanium oxide is most preferred as the nonconductive white powder because its coloring ability is greatest, but others can be used alone or in combination with titanium oxide. 20 ATO and AZO are preferred as the conductive metal oxide for surface coating because they have good covering properties.

As a method of surface coating, a dry method (such as a method in which a conductive metal oxide is deposited by plasma pyrolysis onto a nonconductive white powder in a fluidized bed) is possible, but at present, a wet method is more suitable from 25 an industrial viewpoint. Surface coating by a wet method can be carried out in accordance with the method described in Japanese Patent Publication (Kokoku) No. 60-49136 and U.S. Patent No. 4,452,830, for example. This method will be explained for surface coating with ATO. An alcoholic solution 30 containing hydrolyzable water-soluble salts of antimony and tin (such as antimony chloride and tin chloride) in predetermined proportions is gradually added to a dispersion of a nonconductive white powder (such as titanium oxide powder) in water. The chloride salts are hydrolyzed and the hydrolyzates 35 (precursor of ATO in the form of hydroxides) are co-deposited on the titanium oxide powder so as to coat the powder. After the white powder on which the ATO precursor is deposited is collected and calcined, a white powder coated on its surface

with ATO is obtained.

The amount of surface coating of the nonconductive white powder with the transparent or white conductive metal oxide is preferably such that the volume resistivity (measured at 100 kg/cm²) of the white powder after surface coating is reduced to 10⁴ Ω.cm or less. The amount of coating is generally 5 - 40 wt% relative to the nonconductive white powder and preferably in the range of 10 - 30 wt%.

The amount of conductive materials used in the conductive polymer composition of this invention, in wt% based on the total weight of the composition, is at least 0.01% and less than 2%, preferably 0.05 - 1.5%, and more preferably 0.1 - 1% for the hollow carbon microfibers, and is 2.5 - 40%, preferably 5 - 35%, and more preferably 7.5 - 30% for the electrically conductive white powder. The larger the amount of the hollow carbon microfibers, it is preferable to also increase the amount of the electrically conductive white powder in order to counteract blackening. As a result, the electrical conductivity of the composition becomes high. Therefore, the amount of the hollow carbon microfibers can be selected in accordance with the electrical conductivity required for the use.

If the amount of the hollow carbon microfibers is less than 0.01%, it becomes difficult to impart sufficient electrical conductivity to the polymer, even if a conductive white powder is also added. On the other hand, if the amount is 2% or more, the blackening of the polymer composition becomes noticeable, and it becomes difficult to produce whitening or coloration even if a conductive white powder is present. If the amount of the conductive white powder is less than 2.5%, whitening or coloration becomes difficult, and the electrical conductivity also decreases. If the amount exceeds 40%, the amount of powder is too great, and the moldability of the polymer and the properties, particularly mechanical properties, of the molded product deteriorate.

When the conductive white powder contains a high aspect ratio powder (whether it consists solely of the high aspect ratio powder or is a mixture of that powder with a roughly

spherical powder), the high aspect ratio powder has a tendency to impart directionality to the polymer. In order to avoid excessive directionality, the amount of high aspect ratio powder is preferably at most 35% and particularly at most 25%.

5 When only a conductive white powder is mixed with a polymer to impart electrical conductivity according to a conventional manner, it is necessary to use a large amount of the conductive white powder, i.e., at least 50% of the composition and preferably at least 60% in order to obtain
10 sufficient electrical conductivity. In the present invention, by simultaneously using hollow carbon microfibers in a small amount of less than 2%, electrical conductivity is imparted primarily by the carbon fibers, so the amount of the conductive white powder can be reduced to the amount necessary for
15 whitening. As a result of greatly reducing the amount of this pigment, it is possible to improve the polymer properties. Furthermore, even when the white powder has a high aspect ratio, a high directionality can be prevented, and good moldability can be maintained.

20 The reason that the electrical conductivity of the polymer can be increased by as little as less than 2% of carbon fibers is because hollow carbon microfibers are, as described above, extremely slender and hollow. Electrical conduction occurs along the contact points between the electrically conductive
25 materials. Therefore, the more slender and the lower the bulk specific gravity (hollowness contributes to a low bulk specific gravity), the more contact points between fibers per unit weight. In other words, electrical conductivity can be imparted with a smaller amount of electrically conductive
30 fibers. The hollow carbon microfibers used in this invention are extremely fine with a fiber outer diameter of at most 0.07 μm (70 nm), and normally at most several tens of nanometers, and they have a low specific gravity due to being hollow, so the number of contact points between fibers per unit weight
35 increases, and they can impart electrical conductivity in as small an amount as less than 2%.

Furthermore, the hollow carbon microfibers act as conducting wires linking the electrically conductive white

powder. Namely, even if particles of the white powder are not directly contacting, electrical contact is maintained by the hollow carbon microfibers, and this is thought to further contribute to electrical conductivity.

5 The hollow carbon microfibers used in the present invention have an outer diameter of at most 70 nm, which is shorter than the shortest wavelength of visible light. Therefore, visible light is not absorbed and passes through them, so it is thought that when present in a small amount of 10 less than 2%, the presence of the carbon fibers does not substantially affect the whiteness. Furthermore, as stated above, the amount of the carbon fibers is not large enough to produce directionality of the polymer, so the moldability is not impeded.

15 In Japanese Patent Laid-Open (Kokai) Application No. 3-74465, a polymer composition is made jet black by using 0.1 - 5 wt%, based on the weight of the composition, of hollow carbon microfibers (carbon fibrils), and it is written that mixing of at least 2 wt% is desirable to impart electrical conductivity. 20 In contrast, in the present invention, when less than 2 wt% is used, the color does not become jet black, and electrical conductivity can be imparted. The cause of the difference is thought to be that in the composition of the above-mentioned Japanese Kokai application, at least 50 wt% of the hollow 25 microfibers are present in the form of aggregated fibers forming an aggregate of 0.10 - 0.25 mm, so a large amount of fibers is necessary to obtain electrical conductivity, and even a small amount strongly blackens the polymer. In contrast, in the present invention, the hollow carbon microfibers are 30 dispersed throughout the entire polymer. It is conjectured that due to the dispersion of the fibers and the presence of the electrically conductive white powder, when the hollow carbon microfibers are present in an amount of less than 2 wt%, blackening of the polymer composition is counteracted by the 35 action of the white powder, and a high electrical conductivity is imparted.

The polymer used in the moldable composition according to this invention is not critical as long as it is a moldable

resin, and it can be a thermoplastic resin or a thermosetting resin. Examples of suitable thermoplastic resins are polyolefins such as polyethylene and polypropylene, polyamides such as Nylon 6, Nylon 11, Nylon 66, and Nylon 6,10, polyesters such as polyethylene terephthalate and polybutylene terephthalate, and silicones. In addition, acrylonitrile, styrene, and acrylate resins, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyketones, polyimides, polysulfones, polycarbonates, polyacetals, fluoroplastics, etc. can be used.

Examples of thermosetting resins which can be used in the composition of the present invention are phenolic resins, urea resins, melamine resins, epoxy resins, and polyurethane resins.

Mixing of the conductive materials (fiber and powder) with the polymer can be performed using a conventional mixing machine such as a heated roll mill, an extruder, or a melt blender which can disperse the conductive materials in the polymer in a melt or softened state. The hollow carbon microfibers and the electrically conductive white powder as the conductive materials can each be a mixture of two or more classes. The composition obtained by mixing can be shaped into a suitable formed such as pellets or particles, or it can be immediately used for molding as is.

In addition to the above-described components, the conductive polymer composition of this invention may contain one or more conventional additives such as dispersing agents, coloring agents (white powder, colored pigments, dyes, etc.), charge adjusting agents, lubricants, and anti-oxidizing agents. There are no particular restrictions on the types and amounts of such additives.

Addition of white powder as a coloring agent increases the whiteness of the composition. Addition of one or more colored pigments and/or dyes makes it possible to impart any desired color to the polymer composition of this invention.

There are no particular restrictions on the molding method for the conductive polymer composition according to the present invention or on the shape of the formed product. Molding can be performed by any suitable method including melt spinning,

extrusion, injection molding, and compression molding, which can be appropriately selected depending on the shape of the article and the type of the resin. A melt molding method is preferred, but solution molding method is also possible in some 5 cases. The shape of the articles can be filaments, films, sheets, rods, tubes, and three-dimensional moldings.

When the conductive polymer composition of the present invention does not contain a coloring agent, a formed product having a whiteness of at least 40 and preferably at least 50 10 can be obtained. If the whiteness is at least 40, coloring to a desired color with good color development can be performed by adding a coloring agent.

The product formed using a conductive polymer composition according to this invention in general has a volume resistivity 15 of $10^0 - 10^{10} \Omega \cdot \text{cm}$ and preferably $10^1 - 10^8 \Omega \cdot \text{cm}$ and a surface resistance of at most $10^{10} \Omega/\square$ and preferably $10^2 - 10^9 \Omega/\square$. In the case of filaments, it has an excellent electrical conductivity of at most $10^{10} \Omega$ per centimeter of filament.

Due to this excellent electrical conductivity, a 20 conductive polymer composition according to this invention can be used in any application in which antistatic or electromagnetic wave-shielding properties are necessary. For example, the composition of this invention can be used to manufacture IC trays which are differentiated by color 25 according to the type of product. Furthermore, in the manufacture of antistatic mats, building materials for clean rooms and the like, packaging materials for film, electromagnetic wave shielding materials, dust-free clothing, electrically conductive members, etc., aesthetically attractive 30 products can be manufactured by coloring them to any desired color.

By combining the conductive polymer composition of this invention with a nonconductive polymer, a composite shaped product can be manufactured. For example, as described in 35 Japanese Patent Laid-Open (Kokai) Application No. 57-6762, a conductive polymer composition according to this invention and a common nonconductive polymer can be melt-spun together through a conjugate fiber spinneret having at least two

orifices, and a conjugate filament having a conductive part and a nonconductive part in its cross section can be spun. Using such conjugated filaments, an antistatic fiber product (such as an antistatic mat, dust-free clothing, and carpets) having a drape better than those formed of conductive filaments which are entirely composed of a conductive polymer composition can be manufactured. In the case of films and sheets, the composition can be laminated with a nonconductive polymer.

Examples

10 The following examples are presented to further illustrate the present invention. These examples are to be considered in all respects as illustrative and not restrictive. In the example, all parts and % are by weight unless otherwise specified.

15 The electrically conductive materials used in the examples were as follows.

1. hollow carbon microfibers - Graphite Fibril BN and CC (tradenames of Hyperion Catalysis International, Inc.).

Graphite Fibril BN is a hollow fiber with an outer diameter of 20 0.015 μm (15 nm), an inner diameter of 0.005 μm (5 nm), a length of 0.1 - 10 μm (100 - 10,000 nm), and a volume resistivity in bulk (measured under a pressure of 100 kg/cm²) of 0.2 $\Omega\cdot\text{cm}$. Graphite fibril CC is a hollow fiber with an outer diameter of 0.015 μm (15 nm), an inner diameter of 0.005 μm (5 nm), a length of 0.2 - 20 μm (200 - 20,000 nm), and a volume resistivity in bulk of 0.1 $\Omega\cdot\text{cm}$.

30 2. ATO-coated titanium dioxide powder: Spherical titanium oxide powder (W-P made by Mitsubishi Materials, average particle diameter of 0.2 μm and a specific surface area of 10 m²/g) coated with 15% ATO. It had a volume resistivity of 1.8 $\Omega\cdot\text{cm}$ at a pressure of 100 kg/cm² and a whiteness of 82.

35 3. ATO-coated fluoromica powder: Synthetic fluoromica powder (W-MF made by Mitsubishi Materials, average particle diameter of 2 μm , aspect ratio of 30, specific surface area of 3.8 m²/g) coated with 25% ATO. It had a volume resistivity of 20 $\Omega\cdot\text{cm}$ at a pressure of 100 kg/cm² and a whiteness of 81.

4. AZO powder: Spherical Al-doped zinc oxide powder (23-K made by Hakusui Chemical, average particle diameter of 0.25 μm ,

volume resistivity of $10^2 \Omega \cdot \text{cm}$ at a pressure of 100 kg/cm^2 , and a whiteness of 75).

5. Electrically conductive carbon black (abbreviated CB) (#3250 made by Mitsubishi Chemical, average particle diameter of 28 nm), which was used as a comparative carbonaceous electrically conductive material.

The following materials were used as a polymer.

1. Low-density polyethylene resin (Showlex F171 made by Showa Denko).

10 2. Nylon 6 (Novamide 1030 made by Mitsubishi Chemical).

3. Silicone rubber (X-31 made by Shin-Etsu Chemical).

15 The surface resistance in the examples was the value measured with an insulation-resistance tester (Model SM 8210 made by Toa Denpa). The volume resistivity was the value measured with a digital multimeter (Model 7561 made by Yokogawa Electric). Whiteness was measured using a colorimeter (Color Computer SM7 made by Suga Testing Instruments).

Example 1

20 1 part of hollow carbon microfibers (Graphite Fibril BN), 29 parts of ATO-coated titanium dioxide powder, and 70 parts of polyester resin were melt-blended in a roll mill at 175°C so as to distribute the fibers and the powder uniformly in the resin. The resulting conductive polymer composition was pelletized, and the pellets were melt-extruded into a $75 \mu\text{m}$ -thick film.

25 The resulting white conductive film had a surface resistance of $2 \times 10^5 \Omega/\square$ and a whiteness of 49.

30 The above procedure was repeated to form a conductive white film while varying the amount of the conductive materials or by omitting the hollow carbon microfibers or by using conductive carbon black instead. The results and the composition are shown in Table 1.

The results of another series of test runs in which Graphite Fibril CC was used as the hollow carbon microfibers are shown in Table 2.

35 As can be seen from the above tables, when hollow carbon microfibers were not employed, the film had a high whiteness, but electrical conductivity could not be developed. In contrast, by adding but a minute quantity of 0.5 - 1.5% of

hollow carbon microfibers, the film had a sufficient electrical conductivity while a whiteness of at least 40 was maintained. On the other hand, when the same amount of carbon black was added instead of hollow carbon microfibers, electrical conductivity was not attained, and the film was essentially black.

Table 1

Run No.	Composition (wt%)				Surface Resist. Ω/\square	Whiteness	
	Resin	GF	CB	ATO			
1	70	0.5	—	29.5	3×10^8	53	TI
2	70	1.0	—	29.0	2×10^5	49	TI
3	70	1.5	—	28.5	9×10^3	44	TI
4	70	—	—	30	$> 10^{12}$	71	CO
5	70	—	1	29.0	$> 10^{12}$	21	CO

Resin : Polyethylene, GF = Graphite Fibril BN
 CB = Carbon Black, ATO = ATO-coated titanium oxide powder
 TI = This Invention, CO = Comparative

Table 2

Run No.	Composition (wt%)				Surface Resist. Ω/\square	Whiteness	
	Resin	GF	ATO	Mica			
1	70	0.5	29.5	—	1×10^8	55	TI
2	70	1.0	29.0	—	6×10^3	51	TI
3	70	1.5	28.5	—	7×10^2	44	TI
4	65	0.5	24.5	10	5×10^5	54	TI

Resin : Polyethylene, GF = Graphite Fibril CC
 ATO = ATO-coated titanium oxide powder
 Mica = ATO-coated synthetic fluoromica
 TI = This Invention

Example 2

0.5 parts of hollow carbon microfibers (Graphite Fibril CC), 24.5 parts of ATO-coated titanium dioxide powder, and 75 parts of Nylon 6 resin were melt-blended at 250°C in a twin-screw extruder. The resulting conductive polymer composition

was pelletized, and the pellets were melt-spun through a melt spinning machine to form 12.5 denier Nylon filaments. The resulting filaments had an electrical resistance of $4 \times 10^8 \Omega$ per cm of filament and a whiteness of .52.

- 5 The above process was repeated while varying the amount of the conductive materials or by substituting carbon black for hollow carbon microfibers. The results and the blend compositions are shown in Table 3.

Table 3

Run No.	Composition (wt%)				Electric Resist. Ω/cm	White-ness	
	Resin	GF	CB	ATO			
1	75	0.5	—	24.5	4×10^8	52	TI
2	70	1.0	—	29.0	5×10^6	44	TI
3	70	—	1.0	29.0	$> 10^{12}$	28	CO
4	40	—	1.0	59.0	7×10^{10}	35*	CO

Resin : 6 Nylon, GF = Graphite Fibril CC

CB = Carbon Black, ATO = ATO-coated titanium oxide powder

TI = This Invention, CO = Comparative

* Breakage of filaments occurred during spinning

- By comparing Tests Nos. 2 and 3, it can be seen that
10 electrical conductivity was not obtained when hollow carbon microfibers were replaced by the same amount of carbon black. On the other hand, as shown in Run No. 4, if the amount of electrically conductive white powder was increased to 50% or more, electrical conductivity was exhibited, but the electrical conductivity was lower than for the present invention.
15 Moreover, due to blending a large amount of powder, breakage of filaments occurred during melt spinning, and the moldability was greatly decreased.

Example 3

- 20 0.075 parts of hollow carbon microfibers (Graphite Fibril CC), 19.925 parts of ATO-coated titanium oxide powder, and 80 parts of silicone rubber were uniformly mixed in a roll mill to obtain a semi-fluid conductive polymer composition which is suitable as a conductive sealant, for example. The volume

resistivity of this rubbery composition was $9 \times 10^9 \Omega \cdot \text{cm}$ and it had a whiteness of 69.

The above process was repeated while varying the amount of the electrically conductive materials or by also including ATO-coated fluoromica powder in the electrically conductive materials to obtain a conductive polymer composition. The results and the composition of the blend are shown in Table 4. Electrical conductivity was obtained using only 0.075% of hollow carbon microfibers. It can also be seen that simultaneous use of flake-shaped electrically conductive white powder is effective.

Table 4

Run No.	Composition (wt%)				Volume Resist. $\Omega \cdot \text{cm}$	Whiteness	
	Resin	G F	ATO	Mica			
1	80	0.075	19.925	—	9×10^9	69	TI
2	80	0.3	19.7	—	3×10^6	51	TI
3	80	1.0	19.0	—	7×10^2	42	TI
4	65	1.8	33.2	—	7×10^0	41	TI
5	90	0.3	9.7	—	8×10^6	46	TI
6	70	0.3	9.7	20	3×10^5	58	TI

Resin : Silicone rubber, GF = Graphite Fibril CC

ATO = ATO-coated titanium oxide powder

Mica = ATO-coated synthetic fluoromica

TI = This Invention

Example 4

0.3 parts of Graphite Fibril CC, 34.7 parts of AZO powder, and 65 parts of silicone rubber were uniformly mixed in a roll mill to obtain a semi-fluid conductive polymer composition similar to that of Example 3. This rubbery composition had a volume resistivity of $8 \times 10^6 \Omega \cdot \text{cm}$ and a whiteness of 55.

The above process was repeated while varying the amount of the electrically conductive materials to prepare a conductive polymer composition. The results and the blend composition are shown in Table 5. Even when the white powder was AZO powder which itself is electrically conductive, a high whiteness and electrical conductivity could be obtained.

Table 5

Run No.	Composition (wt%)			Volume Resist. $\Omega \cdot \text{cm}$	White- ness	
	Resin	GF	AZO			
1	65	0.3	34.7	8×10^6	55	TI
2	65	1.0	34.0	1×10^3	43	TI

Resin : Silicone rubber. GF = Graphite Fibril CC

AZO = Al-doped zinc oxide powder

TI = This Invention

Industrial Applicability

Even though an electrically conductive polymer composition of this invention contains hollow carbon microfibers which are a class of carbon fibers, the amount thereof is limited to less than 2 wt%, and by the concurrent presence of an electrically conductive white powder, blackening due to the carbon fibers is suppressed, and it can form molded products having a white outer appearance and excellent electrical conductivity. The conductive polymer composition can be white or can be freely colored to a desired color by use of a coloring agent to give aesthetically attractive conductive products.

Furthermore, by including hollow carbon microfibers which impart high electrical conductivity, the amount of electrically conductive white powder can be decreased, and a deterioration in the physical properties of molded product due to a large amount of conductive powder can be avoided. Since the amount of carbon fibers is small, a decrease in moldability can also be avoided. In addition, the conductive materials produces a reinforcing and packing effect, and the resulting molded product has excellent mechanical properties such as dimensional stability and tensile strength.

Thus, the conductive polymer composition can be used to manufacture various products having antistatic or electromagnetic wave-shielding functions, and it can be used to manufacture products which have an attractive appearance or which can be differentiated by color.

Claims

1. A white, electrically conductive polymer composition comprising a moldable organic polymer having dispersed therein hollow carbon microfibers and an electrically conductive white powder.
2. A colored, electrically conductive polymer composition comprising a moldable organic polymer having dispersed therein hollow carbon microfibers, an electrically conductive white powder, and a coloring agent.
- 10 3. An electrically conductive polymer composition according to claim 1 or 2 wherein the hollow carbon microfibers are present in an amount of at least 0.01 wt% and less than 2 wt% and the electrically conductive white powder is present in an amount of 2.5 - 40 wt%, both based on the total weight of
15 the composition.
4. An electrically conductive polymer composition according to any one of claims 1 to 3 wherein the hollow carbon microfibers have an outer diameter of 3.5 - 70 nm and an aspect ratio of at least 5.
- 20 5. An electrically conductive polymer composition according to any one of claims 1 to 4 wherein the electrically conductive white powder has a volume resistivity (measured at 100 kg/cm²) of at most 10⁴ Ω·cm and a whiteness of at least 70.
- 25 6. An electrically conductive polymer composition according to claim 5 wherein the electrically conductive white powder is either aluminum-doped zinc oxide powder, or a surface-coated white powder selected from the group consisting of titanium oxide, zinc oxide, silica, aluminum oxide, magnesium oxide, zirconium oxide, an alkali metal titanate,
- 30 aluminum borate, barium sulfate, and synthetic fluoromica having a surface coating with an electrically conductive metal oxide selected from the group consisting of antimony-doped tin oxide, aluminum-doped zinc oxide, and tin-doped indium oxide.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 96/03051

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01B1/24 H01B1/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,90 07023 (HYPERION) 28 June 1990 see the whole document ---	1
A	WO,A,91 03057 (HYPERION) 7 March 1991 see claims 1-5 ---	1,4
A	WO,A,94 25966 (MITCHNICK) 10 November 1994 see claims 1-30 ---	1,6
A	DE,A,44 35 376 (DAI NIPPON TORYO) 27 April 1995 see claims 1-17 -----	1,6

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

16 January 1997

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9007023	28-06-90	AU-B-	642401	21-10-93
		AU-A-	4947390	10-07-90
		CA-A-	2005642	16-06-90
		EP-A-	0451208	16-10-91
		IL-A-	92717	27-02-94
		JP-T-	4504445	06-08-92
		US-A-	5500200	19-03-96
-----	-----	-----	-----	-----
WO-A-9103057	07-03-91	JP-A-	3074465	29-03-91
		AU-B-	649626	02-06-94
		AU-A-	6291190	03-04-91
		CA-A-	2065039	15-02-91
		EP-A-	0491728	01-07-92
-----	-----	-----	-----	-----
WO-A-9425966	10-11-94	AU-A-	6627394	21-11-94
		EP-A-	0698275	28-02-96
-----	-----	-----	-----	-----
DE-A-4435376	27-04-95	JP-A-	7102177	18-04-95
		JP-A-	7242843	19-09-95
		US-A-	5504133	02-04-96
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